PB90-219205

TRANSPORT OF MACROMOLECULES AND HUMATE COLLOIDS THROUGH A SAND AND A CLAY AMENDED SAND LABORATORY COLUMN

Robert S. Kerr Environmental Research Laboratory
Ada, OK

Apr 90

U.S. Department of Commerce
National Technical Information Service
NTIS

PB90-219205

EPA/600/2-90/020

TRANSPORT OF MACROMOLECULES AND HUMATE COLLOIDS THROUGH A SAND AND A CLAY AMENDED SAND LABORATORY COLUMN

by

Candida Cook West
Processes and Systems Research Division
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-90/020	2.
3. RECIPIENT'S ACCESSION NO. PB90 219205/AS	
4. TITLE AND SUBTITLE TRANSPORT OF MACROMOLECULES AND HUMATE COLLOIDS THROUGH A SAND AND A CLAY AMENDED SAND LABORATORY COLUMN	5. REPORT DATE April 1990
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Candida Cook West	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Processes and Systems Research Division Robert S. Kerr Environmental Research Laboratory P.O. Box 1198 Ada, OK 74820	10. PROGRAM ELEMENT NO. ABPC1A
	11. CONTRACT/GRANT NO. In-house
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory U.S. Environmental Protection Agency P.O. Box 1198 Ada, OK 74820	13. TYPE OF REPORT AND PERIOD COVERED Final Report
	14. SPONSORING AGENCY CODE EPA/600/15
15. SUPPLEMENTARY NOTES Project Officer: Candida Cook West, FTS: 743-2257	

16. ABSTRACT

Laboratory experiments were conducted to determine if macromolecules or humate colloids would transport through sand columns and if they would exhibit any variations in their relative velocity based upon their molecular volumes and the pore size distribution of the column packing. Poly(ethylene oxide) standards ranging in molecular weights from 50,400 to 900,000 were investigated. Humate colloids were prepared from a humate muck as their calcium and sodium salts. Columns were packed with a fine-grained sand of uniform pore size (≈ 20 μm in diameter) and the same sand amended with 8% clay (4% each kaolinite and illite) resulting in a pore size distribution in which ≈10% of the pores had diameters less than 2 μm. The poly(ehtylene oxides) and calcium and sodium humate colloids were transported virtually conservatively through the Oil Creek sand, with no evidence of size exclusion phenomena. Calcium humate was retarded in the amended sand due to complexation with the clay fraction but moved through the column with 77% recovery of the humate mass. The mobilization of clays was observed as a temporary increase in column effluent turbidity and a significant shift in the particle size distribution of the effluent (150 to 450 nm).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 51
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

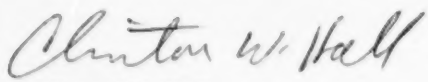
The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This research was conducted for the Office of Ground Water Protection as part of the objectives to protect human health and the environment from ground water contamination. This project report is intended to support this effort by supplementing basic understanding of the mechanisms by, and extent to, which macromolecules and colloids transport in the subsurface.



Clinton W. Hall
Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

Laboratory experiments were conducted to determine if macromolecules, fluorescent microspheres or humate colloids would transport through sand columns and if they would exhibit any variations in their relative velocity based upon their molecular volumes and the pore size distribution of the column packing. Blue dextran, molecular weight 2,000,000, poly(ethylene oxide) standards ranging in molecular weights from 50,400 to 900,000 and 0.05 and 0.51 μm carboxylated and 0.13 and 0.487 μm neutral polystyrene latex particles were investigated. Humate colloids were prepared from a humate muck as their calcium and sodium salts. Columns were packed with fine-grained Oil Creek sand (OCS) of uniform pore size (≈ 20 μm in diameter) and the same sand amended with 4% each kaolinite and illite resulting in a pore size distribution in which ≈ 10% of the pores had diameters less than 2 μm. Blue dextran transported conservatively through the OCS with the average linear velocity of the pore water. Early breakthrough was observed in the amended OCS (0.296 pore volumes before the tritiated water), but only after the column was pre-saturated with blue dextran. The exclusion of the blue dextran could not be explained by either steric exclusion or hydrodynamic velocity gradients. It is possible, however, that diffusional non-equilibrium may be a contributor. The poly(ethylene oxides) and calcium and sodium humate colloids were transported virtually conservatively through the OCS, with no evidence of size exclusion phenomena. Calcium humate was retarded due to complexation with the clay fraction of the amended sand but moved through the column with 77% recovery of the humate mass. The mobilization of clays was observed as a temporary increase in column effluent turbidity and a significant shift in the particle size distribution of the effluent (150 to 450 nm).

The data presented here neither supports nor refutes the application of chromatographic principles to particle transport in soil columns. The behavior of the blue dextran in the amended OCS may be unique. The relative velocities of macromolecules and colloids investigated were not described using a simplistic model discussed in this study. Subsequent studies may need to include diffusional non-equilibrium conditions and solid surface to particle interactions.

This report covers a period from February, 1988 to February, 1990 and work was completed as of April, 1990.

CONTENTS

Disclaimer ii
Foreword iii
Abstract iv
Abbreviations and Symbols vi
Acknowledgements vii

I. Introduction 1

II. Background 1

III. Theoretical Development 5

IV. Conclusions 7

V. Materials and Methods

A. Polymers and Macromolecules 8
B. Columns 9
C. Column Packing 10
D. Analytical Methods 10

VI. Results and Discussion

A. Pore Size Frequency Distributions 12
B. Particle Size Distributions 12
C. Column Breakthrough and
Batch Sorption Studies 13

1. Blue Dextran 13
2. Poly(ethylene oxides) 14
3. Humate Colloids 14
4. Fluorescent Microspheres 15

Figures 16
Tables 38
References 40

ABBREVIATIONS AND SYMBOLS

V_D = Darcy velocity

$\bar{v}_w$ = interstitial velocity of water
= V_D/θ_t where θ_t = total saturated volume

$\bar{v}_{p,w}$ = interstitial velocity of a particle of radius, r

$\bar{v}_{p,\varepsilon}$ = excluded interstitial velocity of a particle
= V_D/θ_ε where θ_ε = total available saturated volume

OCS = Oil Creek sand

AOCS = Clay amended Oil Creek sand

ACKNOWLEDGEMENTS

I acknowledge the participation of Dr. Narong Chamkasem, and Ms. Lynda Pennington of NSI (RSKERL) for their assistance in the analysis of poly(ethylene oxides) and organic carbon. I also thank Dr. Jong Soo Cho for his contributions to the theoretical development of size contributions to particle velocity.

I. INTRODUCTION

Evaluating contaminant fate in any environment necessitates determining the compartments into which the contaminant will distribute. In saturated subsurface environments the partitioning of a contaminant between the mobile aqueous phase and the immobile aquifer solid matrix is often the controlling distribution. The association of a contaminant with immobile solids results in a reduction in the dissolved mobile concentration of the contaminant, sometimes by orders of magnitude. However, it has been suggested that mobile entities such as suspended organic and inorganic colloids and macromolecules may increase the "apparent" solubility of some contaminants (Abdul *et al.* 1990; Penrose *et al.*, 1990; Puls and Barcelona, 1989; Enfield and Bengtsson, 1988; Chiou *et al.*, 1987). If this is the case, then predictions of contaminant transport based upon a two-phase system may seriously underestimate observed aqueous phase concentrations of contaminant in laboratory and field studies. The influence of these entities would need to be addressed by modeling systems as three phases consisting of immobile sorbed, dissolved and mobile sorbed phases.

There is a good deal of research activity in the areas of colloid origination, chemistry, stability and mobility. Recently, colloidal entities such as macromolecules and viruses have been observed to be capable of eluting prior to conservative solutes in column and field studies. The intent of this study was to observe the transport of colloid-sized entities and to examine the validity of two proposed mechanisms by which this phenomenon may occur in the subsurface.

II. BACKGROUND

Definition of Colloidal Phases

Macromolecules, sometimes referred to as molecular colloids, are colloidal by virtue of their size, interactions with other molecules and colloidal phenomena such as swelling, precipitation, sorption, flocculation and micelle formation (Breger, 1970). Macromolecules can be loosely defined as those molecules whose molecular weight exceeds 10,000 and may range in diameter from one to several hundred nanometers.

The definition of a colloid is unclear because it is not strictly solute or solid. Colloid-associated contaminants cannot be considered "truly" dissolved. They cannot be considered part of the immobile solid matrix because they do not settle out and are carried with the mobile phase. Strictly speaking, a colloidal system is comprised of a dispersing medium and a suspended dispersed phase (colloid). Colloidal systems are solid/liquid, liquid/liquid or gas/liquid. In the case of solid/liquid systems, the colloid is a hydrated solid held in suspension and treated as a solute. One recommended definition of colloids is those species or particles subject to Brownian motion with a size between 0.001 - 10 μm (Buddemeier and Hunt, 1988; Stumm, 1977). Another

useful, but rarely used, definition of a colloid that addresses long-chained linear and highly asymmetrical colloids is that of a particle containing approximately one thousand to one billion atoms (Jirgensons, 1958). An empirical definition of colloids recognized in this research includes those phases that cannot be separated from solution by conventional means such as gravity settling, filtration (0.45 μm) or standard centrifugation.

Size is not the only consideration to be made when classifying a particle or macromolecule as a colloid. Defined size limitations are made on the assumption of spherical shape; but for other tertiary shapes, charge density is a determining factor. The higher the specific surface charge, the larger the particle can be and still exhibit colloidal behavior. Extremely high surface area to volume ratio is essential to colloidal stability in most cases.

Colloids in the Subsurface Environment

Colloidal systems of environmental interest are primarily solid/liquid (clay, bacteria, viruses, precipitates) and liquid/liquid (micelles and macromolecules of molecular weight > 10,000). A gas/liquid colloidal system may exist in some cases of vapor transport in unsaturated systems. Colloids may be formed in situ by condensation or homogeneous nucleation of particles from dissolved species when a mineral phase is supersaturated or release of particles from bulk material into a suspension of particulate solids (Buddemeier and Hunt, 1988; Apps *et al*, 1982). The latter mechanism is likely largely responsible for considerable artifacts in compiling experimental partition coefficients and desorption kinetics. Colloids may be introduced into a system by virtue of being a component in original source of pollution. A scenario exemplifying this would be wood pulp wastes or the wasting of polymeric materials. Water-soluble polymer additives used in oil well drilling fluids form hydrocolloids that may be mobile. That is, they hydrate, swell and disperse in water rather than dissolve (Lauzon, 1982). The chemistry, formation and environmental significance of colloids in the subsurface environment has been reviewed extensively by McCarthy and Zachara (1989).

Examples of typical colloids and colloid-sized particles that may be mobile in the subsurface are metal oxides and hydroxides, clay particles, viruses and bacteria, and indigenous organic macromolecules. Less typical would be synthetic macromolecules such as the high molecular weight polymers that are in prevalent use today. Mobilization of clay fines or organic carbon when destabilized by low ionic strength eluents or changes in counterion is a common experience when conditioning a laboratory soil column. Colloids are typically generated in response to sudden changes in geochemistry. Changes in pH, pE and ionic strength are common as wastes or meteoric water percolate through a formation. There is substantial evidence that colloids can move with the average linear ground water velocity and can significantly impact the mobility, and sometimes the toxicity, of contaminants that otherwise would be considered too highly retained by the solid matrix to be of concern. An excellent literature review and description of mechanisms of particle release and capture is presented by McDowell-Boyer *et al.* (1986).

Gschwend and Reynolds (1987), using SEM and SEM-EDAX analysis, found monodisperse (100 nm) colloidal materials consisting primarily of iron and phosphorus in ground water samples collected 300 meters downgradient and 11 meters below the water surface of a secondary-sewage infiltration site on Cape Cod, Masschusetts. These colloids apparently were formed in situ in response to oxygen depletion and were speculated to be mobile. Organic macromolecules in the influent (6 ± 3 nm diameter) appeared not to be transported independently in the system. However, it was hypothesized that they may have coated the positively charged surfaces of the ferrous phosphate particles, thus preventing them from coagulating or filtering out of the system. Under pristine conditions, there can be movement of colloids induced by rain events. For instance, Murphy et al. (1989) determined by isotopic composition that the high molecular weight fractions of indigenous dissolved organic carbon (DOC) in samples taken from the Milk River aquifer in Alberta, Canada were mobile and originated in the interstitial waters of the soil zone in the area of recharge. Organic and inorganic colloids ranging in sizes from 0.04 to 1 μm have been found to be mobile in a subsurface fracture in granitic rock (Degueldre *et al.*,1989). The nature of the colloids was highly complex, with the inorganic colloids being comprised of Si, Ca, Mg, Sr, Ba, Fe and S. A threshold level of 5 mg/l has been suggested by Leenheer *et al.* (1974) to differentiate between indigenous and introduced organic carbon. This was established by analyzing base levels of naturally occurring DOC from 100 sites in 27 states.

Implications of Colloid Formation

Regardless of the origin, conditions which lead to the destabilization of the solid matrix to form colloids or precipitation of sparingly soluble molecules from the aqueous phase may occur until the plume is diluted such that its geochemistry readjusts to the environment. Increases in ground water turbidity in response to artificial low salinity ground water recharge has been observed at many field sites, some of which were studied as early as 1969 (Nightingale and Bianchi, 1977). The size of the particles that were transported indicate that the probability for filtration and interaction of particles may be a function of whether the particles were introduced from outside the system or generated from the system.

The literature suggests that colloid function has added implications with respect to contaminant transport. There have been numerous publications concerning the partitioning and reactions of hydrophobic organic compounds to dissolved humic materials and micelles greatly increasing the solute aqueous solubility (Kan and Tomson, 1990; Kile and Chiou, 1989; Valsaraj and Thibodeaux, 1989 and Schnitzer *et al.*, 1988). It is not known if the humates responsible for increases in apparent solute solubilities exist as macromolecules of discrete units or aggregated units operating essentially as micelles (Wershaw, 1986). Buddemeier and Hunt (1988) hypothesized that colloid-bound nuclides exhibit reduced mobility as compared to free nuclides. This may be due to increased interactions with the environment as the bound species. Penrose *et al.* (1990) found that plutonium and americium species were mobilized by colloidal material

between 25 and 450 nm in size and transported to monitoring wells 3390 meters downgradient from the source.

There are practical implications to interactions between colloids and contaminants. One implication concerns well sampling. It has been argued that the standard method for differentiating between free and bound metals by 0.45 μm filtration may be inappropriate (Puls and Barcelona, 1989). The presence of metals associated with colloids less than 0.45 μm would result in erroneously high dissolved concentrations. The argument may apply to organic contaminants as well. Another implication relates to the use of colloids for remediation. The possibility of using humate colloids to facilitate the removal of contaminants from soil has been suggested in a recent study where a solution of 29 mg/L humic acid more effectively removed non-polar organic compounds than did water (Abdul *et al.*, 1990). Further studies on the interaction between previously sorbed contaminants and humic materials is warranted. There would be significant advantages using natural humate colloids for remediation since they are cheaper and more environmentally acceptable than commercially prepared surfactants.

There has been evidence to suggest that the toxicity of contaminants may be greatly reduced when associated with colloids or organic macromolecules. Black and McCarthy (1988) found that when benzo(a)pyrene and 2,2',5,5'-tetrachlorobiphenyl were bound to dissolved Aldrich humic acid, they did not diffuse across the gill membrane of rainbow trout. It has also been observed that when gold is bound to commerically prepared (Aldrich) humic acid it is unavailable for soil cycling (Jones and Peterson, 1989). However, it may not be appropriate to extrapolate the extent of sorption of hydrophobic compounds to commercial humic acid to real world situations (Chiou *et al.* 1987).

Suspended colloids are subject to physical and chemical mechanisms that can limit their transport in porous media. Two physical mechanisms leading to removal of colloids are surface and straining filtration and are a function of the particle/pore diameter ratio. In the case of surface filtration, particle accumulation leads to significant reduction in formation permeability. Physical-chemical filtration is also a function of particle and media surface charges. Mobilization of quartz fines during oil production by fluid injection has been found to be dependent on both ionic strength and the pH of injection fluid and virtually independent of fines size (Cerda, 1988). Physical-chemical interactions of stable particles to media surfaces often are not considered to result in permeability reduction because there is only monolayer coverage. Destabilized colloids can, however, create a situation where particle-particle interactions are sufficient such that the thickness of deposition may cause a reduction in permeability.

In an investigation conducted by Smith *et al.* (1985), it was shown that when an intact soil core was sieved and repacked, *E. coli* transport was reduced from 22-79% to 0.2-7% penetration. All other conditions being held equal, this indicated that the pathway was by way of secondary permeability rather than intergranular pore spaces. However, Bales *et al.* (1989) demonstrated

that bacteriophage are conservatively transported in a homogeneously packed sandy soil column. It was also observed that the phage broke through prior to tritiated water and were excluded from 35 to 45% of the void volume. Enfield and Bengtsson (1988) had previously observed that blue dextran (molecular weight two million) broke through a laboratory column prior to tritiated water and that the relative position of the breakthrough appeared to be dependent on the pore size distribution of a homogeneously packed column. It was hypothesized that this phenomena was a result of the particle/pore diameter ratios as in size exclusion chromatography.

The purpose of this study was first to gather more evidence for organic colloid mobility, both synthetic and natural, and secondly, to examine the validity of proposed mechanisms for early breakthrough observations.

The interstitial velocity of ground water ($\bar{v}_w$) is defined as the Darcy velocity corrected for porosity. By analogy, the intersitital velocity of a mobile particle ($\bar{v}_{p,\varepsilon}$) may be normalized to the porosity it is able to travel.

III. THEORETICAL DEVELOPMENT

For the most part, discussions of colloid and macromolecule transport have been confined to observations influenced by physical and chemical interactions that would retard their transport, relative to conservative species. As discussed in the previous section, there may be mechanisms by which macromolecules and colloids can elute prior to conservative species as has been observed in laboratory and field studies. Two mechanisms which have been proposed to account for this behavior are discussed.

The first mechanism is that of particle exclusion from pores. Concepts from steric (size) exclusion chromatography (SEC) have been examined with respect to applicability to classic dispersion/advection theory (Peyton *et al.*, 1985; Peyton *et al.*, 1986). A particle may be excluded from dead end pores and pores smaller than some critical diameter based upon the ratio of the particle diameter to pore diameter and flowrates (dynamic porosity). The exclusion from these pores is a function both of molecular volume and fluid velocity, that is, diffusional equilibrium into a pore is a function of the velocity of the fluid as it moves past the pore. This can result in an "effective" porosity for that particle (θ_ε) that may be both specific for the particle (i.e species) involved and less than the total porosity (θ_t). A solute diffusing through less than the total porosity would elute from a soil column prior to a smaller chemical specie like water ($\bar{v}_p = V_D / \theta_\varepsilon > \bar{v}_w = V_D / \theta_t$).

The second mechanism by which the elution velocity of a particle may be a function of its size can be described by analogy to hydrodynamic velocity gradients in capillary flow. Hydrodynamic chromatography (HDC) is an analytical technique used to separate particles based

on their size and rate of transport through a bed packed with solid, non-porous particles. The use of HDC was first described by Small (1974). According to this theory, the rate of transport of conservative colloidal particles depends on the size of the colloid and the inter-particle volume of the column packing. Larger particles move faster than the smaller ones, which in turn move faster than the molecules of the elution fluid (Stoisits, *et al.* 1976). There exists across the flow channel a velocity gradient such that the velocity of the fluid is maximum at the center and diminishes toward the wall. The mean velocity of a particle is a function of the velocity gradient to which it is subjected, based upon the particle radius. A small molecule, such as water, can access the entire gradient; and hence, its average interstitial velocity is $1/2\ v_{max}$. A large particle will be subject to higher velocities than a relatively smaller particle. The rate of transport through a column bed is expressed by the quantity R_f, the average moving rate of a particle through the bed relative to the average flow rate of the mobile phase ($\bar{v}_{p,w} / \bar{v}_w$). R_f is analogous to the relative velocity of a contaminant in groundwater (i.e. velocity of the contaminant/velocity of the water). Stoisits *et al.* (1976) first mathematically verified hydrodynamic chromatography flow based on a model by DiMarzio and Guttman (1969, 1970) derived for rigid and flexible polymer molecules flowing in Poiseuille flow through a capillary tube. The velocity at a point r, v(r), from the center of the capillary in the radius of the tube is given by the equation:

$$v(r) = [(\Delta p r_o^{\,2})/(4\eta\iota)]\,[1-(r/r_o)^2]$$

where

Δp = pressure drop across the capillary
r_o = radius of the cylinder
η = dynamic viscosity of the fluid
ι = total length of the cylinder

and the maximum velocity at r = 0 is

$$v_{max} = (\Delta p r_o^{\,2})/(4\eta\iota) = 2\bar{v}_w$$

Since a particle of radius r_p will be subject only to the portion of the velocity gradient $\geq r_p$ from the wall, the average velocity of the particle ($\bar{v}_{p,w}$) can then be calculated as:

$$\bar{v}_{p,w} = \bar{v}_{max}[1 - 1/2(1-\alpha)^2]$$

where

α = radius of the particle/radius of the pore (r_p/r_o)

This then can be rewritten as:

$$\bar{v}_{p,w} = \bar{v}_{w} [1 + \alpha(2-\alpha)]$$

Based on the theories of size exclusion and hydrodynamic velocity in a system of conservative solutes, those particles not subject to physical straining should transport according to size and fluid velocities and the two mechanisms contributing to particle velocity would be operational. Assuming that the effective porosity is the total pore volume available to an excluded macromolecule and that corrections for the reduced fluid volume in which it travels is insignificant, then the elution velocity of an excluded particle ($\bar{v}_{p,\varepsilon}$) can be approximated:

$$\bar{v}_{p,\varepsilon} = V_d / \theta_\varepsilon$$

where

$$V_d = \bar{v}_w * \theta_t$$

Since the average linear velocity of the excluded particle can be calculated by its hydrodynamic velocity as defined above ($\bar{v}_w = \bar{v}_{p,w}$) we now have:

$$\bar{v}_{p,\varepsilon} / \bar{v}_w = (\theta_t / \theta_\varepsilon) [1 + \alpha(2-\alpha)]$$

Using the guideline that straining will occur at a particle to pore diameter ratio (α) of 1 to 9 (Sakthivodiel, 1969), the limits placed on $\bar{v}_{p,\varepsilon}$ based on the hydrodynamic velocity will be:

$\bar{v}_{p,\varepsilon} / \bar{v}_w = 1.20 (\theta_t / \theta_\varepsilon)$ when $\alpha = 1/9$ and

$\bar{v}_{p,\varepsilon} / \bar{v}_w = 1$ as α approaches zero, θ_ε approaches θ_t.

IV. CONCLUSIONS

Blue dextran, poly(ethylene oxides) of molecular weight 50,400 to 770,000 and humate colloids (150 - 450 µm) transported through a sand column virtually conservatively. The addition of clay to the packing materials introduced solid matrix/macromolecule interactions that significantly retarded or removed blue dextran and poly(ethylene oxides) from solution. Blue dextran eluted from the clay-amended column 0.265 pore volumes prior to the tritiated water. This occurred only after the column was first pre-saturated with blue dextran. This casts serious doubts as to the interpretation of the breakthrough data. Calculation of the relative velocity of the blue dextran through the clay amended column based on hydrodynamic velocity and size exclusion from the smallest pores (R_f = 1.117 - 1.160) underestimated that observed relative velocity (1.265).

The calcium humate colloid was retarded due to irreversible clay-humate interactions. Subsequent flow of calcium humate through the column showed significantly less retardation of the humate. Based on the theories of relative velocity presented here, it would be expected to see early breakthrough of the humate colloids. However, driving the system to saturation would have caused the same doubtful situation as in the case of blue dextran.

An additional observation made in these studies was that the behavior of the tritiated water was erratic as evidenced by data-scatter, breakthrough curve asymmetry and excessive tailing. This may have been due to the equilibrium of water molecules from the bulk phase to the hydrated colloid. If this is the case, then tritiated water may not be an appropriate conservative tracer for the transport studies.

In many ways, the neutral or charged microspheres would have been ideal models for these studies as they can be purchased in a wide range of particle sizes with small standard deviations and specified surface charge. It was observed in these studies, however, that considerable cleaning of the microspheres is necessary to remove interfering contamination of the charge characteristics by surfactants used in the manufacture of the beads. The humate colloids do however present an interesting possibility for further study. Their size can be controlled by variation in pH, ionic strength and counterion, and they are more relevant to subsurface transport studies.

The observation of column transport of the colloids and macromolecules present additional evidence for colloidal mobility. The ability to predict the rate at which these particles transport in media other than non-interactive is highly complex and may ultimately be of minor significance except under very specific circumstances.

V. MATERIALS AND METHODS

A. Polymers and Macromolecules

Blue dextran is a polysaccharide (α 1-6 polyglucose) produced by *Leuconostoc mesenteroides* (B512) and dyed with Cibacron blue . It can be purchased in several different average molecular weights and is used primarily for calibrating gel filtration columns. The blue dextran was purchased from Sigma Chemical Company in 95% purity and two million average molecular weight. The blue dextran concentration in column experiments was 100 mg/L in 0.01 M $CaCl_2$. Experiments were conducted in a controlled temperature room at 12°C. Feed solutions were poisoned with 0.1% by weight NaN_3 to prevent bacterial growth.

Poly(ethylene oxide) polymers have the monomeric formula $(-CH_2CH_2O-)_n$. Standards were obtained from Alltech Assoc. (Deerfield, IL) as a kit containing 0.2 g each of eight

high purity polymers ranging in average molecular weight from 14,200 to 900,000. Poly(ethylene oxides) were prepared in 0.01 M $CaCl_2$ and 0.1% by weight NaN_3. Experimental concentrations of the poly(ethylene oxides) ranged from 961 to 1261 ppm and are given for each experiment in the experimental section.

Humate colloids were prepared from a humate muck that is a produced as a co-product of titanium dioxide mining in Northern Florida. Prior to preparation of colloids for column studies, a series of humate solutions was prepared for the purpose of determining the range of colloidal sizes that could be produced varying solution pH and cation concentration. Two sets of humate solutions were made by adding 1.0 g of humate muck to 1 liter of deionized water and 1 liter of 0.01 M $CaCl_2$. The solutions were weakly buffered to pH 6, 7 and 8 using sulfonic acid buffers (MES, BES and bicine, Sigma Chemical Co., St. Louis, MO).

The humates prepared for experimental purposes contained no buffers as further work showed them to be stable. Additionally, higher concentrations were prepared for analytical reasons. Sodium humate was prepared by weighing 100 grams of humate muck (25% solids by weight as determined by oven drying at 100°C for 24 hours) into 0.01 M $NaClO_4$ and bringing the solution up to a total volume of one liter. The initial pH was 3.92. The solution pH was then adjusted to match that of the background $NaClO_4$ solution, pH 5.76, using 1.0 M NaOH. After stirring overnight, the humate solution was allowed to settle for 24 hours. The supernatant was collected by vacuum suctioning, then centrifuged at 3,000 rpm for one hour and filtered in small aliquots through 0.45µm Millipore filters. The calcium humate was prepared in the same manner, except the diluting solution was 0.01 M $CaSO_4$. The initial pH was 4.04 and was adjusted to 6.41.

Yellow-green fluoresbrite, carboxylated (0.05 and 0.51 µm) and neutral (0.13 and 0.487 µm) polystyrene latex microspheres were purchased from Polysciences, Inc. (Warrington, PA).

B. Columns

Two column types were used in this study. The first consisted of beaded glass pipe (Ace Glassware, Inc., Vineland, NJ) and end caps fitted with threaded glass connectors. The column dimensions were 15.2 cm in length and 5 cm inside diameter. The endcaps were connected to the pipe by coupling-bolts with Teflon liners. The columns were dry-packed to minimize introduction of secondary channels. All blue dextran breakthrough curves were conducted through these columns. Flow in all experiments was from bottom up to ensure saturation.

The second column type was specially fabricated of 316 stainless steel, 1 cm in length and 5.0 cm internal diameter. The columns were fitted with removable stainless steel porous endplates, 0.078 cm thickness and 40 μm pore size (Mott Company, Farmington, CT) and Viton o-rings. These were used for all poly(ethylene oxide) and humate studies, primarily to minimize the quantity and cost of the polymers necessary for the experiments.

Solutions were pumped into the columns by a Technicon auto analyzer proportioning pump using tygon pump tubes. The columns were plumbed to the feed solutions and pump via teflon tubing. Flowrates were 9.6 ml/hour (0.474 cm/hr linear velocity) for all column experiments. Samples were collected into pre-weighed vials by a model 3100 Cygnet fraction collector (ISCO, Inc., Lincoln, NB). After collection, vials were re-weighed for flowrate and volume verification. Appropriate sampling aliquots were taken from the vials for analyses.

C. Column Packing

The column packing material selected for this study is a fine-grained sand referred to as OCS (OCS) mined commercially in Oklahoma. It is comprised of 99.6% sand and 0.4% silt. The total organic carbon content of the sand is 0.0045%. Where noted, the sand was amended with 4% each kaolinite and illite clay standard (8% total clay) obtained from the Clay Minerals Society for the purpose of adjusting the pore size distribution.

D. Analytical Methods

Blue dextran concentrations were analyzed on a Shimadzu DV160 scanning spectrophotometer at 630 nm using proper quality assurance procedures. The poly(ethylene oxides) were analyzed using HPLC gel permeation chromatography. The system was comprised of a Waters model 590 high pressure pump, model 712B auto sampler, model 401 refractive index detector, a column heater module to maintain constant column temperature and a Nelson Analytical microcomputer-base integrator. Ultrahydrogel GPC columns (250, 500 and 1000) were purchased from Waters. The limit of detection for the poly(ethylene oxides) was ≠ 100 ppm. High feed solution concentrations were used in column studies (961-1261 ppm) so that breakthrough could be discerned at ≠ 10% relative concentration and quality control objectives could be met.

Humate concentrations were expressed as mg/L organic carbon determined using low temperature ultraviolet/potassium persulfate oxidation after acidification with concentrated phosphoric acid.

The total organic carbon in column packings was determined by digestion in 10% perchloric acid with subsequent solids analysis by Leco WR-110 and filtrate analysis on a Dohrmann DC-80 using low temperature ultraviolet/potassium persulfate oxidation.

Fatty acid determinations were performed on column effluents as a qualitative indicator of presence or absence of microbial growth in blue dextran and poly(ethylene oxide) column experiments. Column effluents were analyzed for C_3 to C_7 fatty acids by acidic ethyl ether extraction and subsequent analysis by GC/FID using DB-5 capillary columns. The limit of detection was approximately 1 ppm. Standards were purchased from Supelco (volatile acid standard mix).

Particle size distributions were determined on a Malvern Autosizer 2C. Microsphere analysis was by G.K. Turner fluorometer using appropriate primary and secondary filters. Excitation and emission wavelengths are 458 and 540 nm, respectively. The lower detection limit was 1 ppb.

Microspheres were dialyzed against distilled, reverse-osmosis water using Spectra/Por dialysis membrane, 1,000 molecular weight cut-off (Spectrum Medical Industries, Los Angeles, CA). Diafiltration was performed using hollow fiber filters with .01 µm opening and 500 µm diameter (H1P100-20 filter, Amicon Corporation, Danvers, MA).

Tritium concentrations were analyzed on a LKB model 1219 Rackbeta liquid scintillation counter with automatic quench correction. Water soluble Ready Safe scintillation cocktail (Beckman) was used in all experiments. Sample to cocktail ratios varied from 0.1:6 to 1.0:6 ml, respectively.

Soil moisture characteristic curves were performed on both the OCS and amended OCS using standard Tempe cells in which a drainage curve is established by pairing volumetric water content with matric pressure head (American Society for Testing and Materials, F316). From these curves, assuming spherical particles, pore size distributions were calculated using the equation:

$$2\pi r\gamma\cos\theta = r^2\pi(h\rho g)$$

where

r = radius of the pore or capillary

γ = surface tension of water

θ = contact angle ($\cos\theta = 1$ for a wetted sample)

$h\rho g$ = hydrostatic pressure

V. RESULTS AND DISCUSSION

A. Pore Size Frequency Distributions of Column Packings

The interparticle pore size frequency distribution for OCS is very uniform, with ≈74% of the pore radii between 13 to 8 μm and less than 1% ≤ 1.0 μm (figure 1). When the sand was amended with 6% clay (equal weight kaolinite and illite), ≈10% of the pores were less than 1.0 μm (figure 2), which could be expected to provide a significant proportion of pore openings from which a large colloid would be excluded if size exclusion is functional.

B. Particle Size Distributions

The particle size distributions for the study polymers are given in table 1. The blue dextran and poly(ethylene oxides) could only be estimated due to their non-spherical shapes. Nevertheless, the range of particle diameters (≈ 100 to 200 nm) can be used to estimate if there would be any significant effect of molecular volume on breakthrough velocity in either of the column packings used based on the theories described above.

The cumulative particle size distribution (figure 3) for the humate suspensions made at varying pH and counterion had trends in size that are in keeping with observations made by Ghosh and Schnitzer (1980) using surface pressure and viscosity measurements. It appears that the ionic strength of the buffer was sufficient to keep the overall particle sizes small. As a general rule, humate solubility increases with pH due to increasing negative charge; and conformation changes from coiled to linear as the distance between like charges is maximized. Addition of a divalent cation like calcium aggregated humate, which, as in this case, increases the size of the particles. Additionally, the numbers of particles were greater for all the humates in deionized water than those prepared in the calcium solution (data not shown), again indicating humate aggregation. The humate suspension in buffered deionized water had sufficient ionic strength to minimize the effect of pH. Based on this behavior, it was decided not to buffer humate solutions.

The colloids prepared for column studies were examined for particle size distribution, stability of size distribution from one batch preparation to another and over time, and maintainence of distribution after transport through columns. The latter will be discussed with the column results. The calcium humate had a particle size distribution predominantly between 350 to 525 nm and a small contribution in the 200 to 250 nm range. The sodium humate had a significant particle population in the same size distribution as the calcium humate, but was bimodal with a significantly higher population in the range of 200 to 250 nm (figure 4). The particle size distributions of

both humates were stable over a period of five days (figure 5 and 6). The reproducibility of the sodium humate from one batch preparation to the next was good (figure 7), reaffirming that the bimodal distribution was not an artifact.

C. Column Breakthrough and Batch Sorption Studies

Experimental concentrations, recoveries and experimental R_f's for column breakthrough results for the study macromolecules are listed in table 2 for reference.

1. Blue Dextran

Blue dextran transported through the OCS conservatively (98% recovery) and moved at the average interstitial velocity of the bulk fluid (figure 8). Attempts to conduct column studies through the clay amended OCS were unsuccessful due to significant sorptive losses of the blue dextran to the column packing. Batch sorption isotherms were conducted for blue dextran at pH 4.0 and 8.0 to determine if there was any pH dependency. It appeared that the sorption of blue dextran to the clay amended OCS was independent of pH and highly non-linear (log Kd = 4.2; 1/n = 0.24 at pH 8.0, 0.28 at pH 4.0) (figure 9). Batch sorption experiments were then conducted for blue dextran and its components, dextran and cibacron blue. This was done to verify that there was no separation of the chromophore from the dextran. In some manufacturing processes, dyes are only hydrophobically "bound" as opposed to forming covalent bonds. The batch sorption experiments were also run to determine if the dye alone was responsible for the sorption. Sorption for both the dextran and cibacron blue were fairly linear (1/n > 0.9) with log Kd's of 1.6 and .996, respectively. Desorption for both components over 72 hours was minimal (figures 10 and 11). This indicated that both compounds contributed to the sorption of the blue dextran to the clay fraction of the column packing. This was not unexpected as cibacron blue is subject to hydrophobic and ionic interactions of sulfonated and amino groups (personal communication, Sigma Chemical Company) and clay/polysaccharide complexes have been studied (Clapp and Emerson, 1972). However, the column elution behavior of the blue dextran was more complex than that which may have been predicted from linear additive sorption of the two components. Blue dextran was pumped through the amended OCS column until saturated (the effluent and influent concentrations were approximately equal). The column was flushed with background solution until the effluent blue dextran concentration became relatively constant at ≈18 ppm. A pulse of blue dextran in tritiated water was then pumped into the column and the effluent monitored. The blue dextran C/Co = 0.5 eluted from the column approximately 0.296 pore volumes prior to the tritiated water tracer (figure 12).

The relative velocity (R_f) based on hydrodynamic flow is calculated to range between 1.005 to 1.044 for blue dextran in the OCS assuming the macromolecular diameter is 0.076 μm and the pore radius distribution limits are ≈ 3 to 35 μm. If it could be assumed that in the clay amended column blue dextran was completely excluded from those pores < 1 μm in radius, the effective porosity would be reduced 10%, thus increasing the relative velocity to 1.117 to 1.160. The high relative velocity of the blue dextran (1.296) cannot be explained on the basis of hydrodynamic velocity and size exclusion. Its elution behavior may also have been influenced by surface repulsive forces such as in anion exclusion or by diffusional non-equilibrium effects.

2. Poly(ethylene oxides)

Except for 900,000 molecular weight fraction, all the poly(ethylene oxides) broke through the OCS after the tritiated water ($R_f < 1.0$) (figures 13 to 15). Recoveries of the 50.7K, 83.8K and 770K polymers were relatively high (84-98%) although some tailing was observed. The 900,000 molecular weight poly(ethylene oxide) eluted prior to tritium ($R_f = 1.116$). It is difficult to determine if this is real or an artifact, perhaps a reflection of inaccurate analysis as evidenced by the high recovery (109%). No polymer was detected in the effluent when transport studies of two of the polymers through an amended OCS column was conducted. Batch sorption tests (figure 16) showed that due to sorption excessive quantities of the expensive polymers would need to be purchased to conduct further studies. For this reason the column elution studies were not pursued.

3. Humate Colloids

Both the sodium and calcium humates transported conservatively (≈ 100% recovery) through the OCS (figures 17 and 18). The particle size distribution for the sodium humate effluent was virtually identical to that in the influent (figure 19). However, a percentage of the particles in the calcium humate effluent shifted to significantly smaller particle diameters (figure 20), most probably due to calcium ion loss from the humate complex by the low cation exchange capacity of the sand causing disaggregation of the humate particles. The calcium humate was retarded in the amended OCS (figure 21) in an apparently irreversible fashion. Approximately 77% of the humate mass was recovered. The effluent temporarily became turbid and the particle size distribution (figure 22) showed a marked change from a primary particle size of 150 nm to ≈ 450 nm indicating that the elution species was probably a clay/humate complex. There was considerable scatter in the tritium data for this breakthrough curve which was probably due to interference by the clay particles. When calcium humate was pulsed a second time it was observed that the humate

broke through with less retardation, due to saturation of some fraction of the immobile clay sites.

4. Fluorescent Microspheres

Several attempts to conduct column breakthrough curves through OCS were unsuccessful due to interactions of the microspheres with the glass and sand. Electrophoresis qualitatively indicated that the net surface charge of the microspheres at fixed pH was not that provided by the manufacturer. Microscopic examination of the microspheres revealed the presence of bacteria and molds, apparently growing on the surfactant residuals left from the manufacturing process. Dialysis of uncontaminated the 0.05 µm carboxylated microspheres did not adequately reduce interactions between the microspheres and sand, although there was some charge improvement. A final attempt to clean the microspheres by diafiltration was unsuccessful. The beads sorbed to the filter and reversing flow was unsuccessful in removing them. The ionic strength of all solutions were below the manufacturer's stated critical coagulation concentrations. Additionally, microscopic examinations confirmed that the beads were monodisperse. Since no reasonable explanation for this could be made by either supplier (Polysciences or Amicon), no further attempts were made to use the microspheres as colloid surrogates.

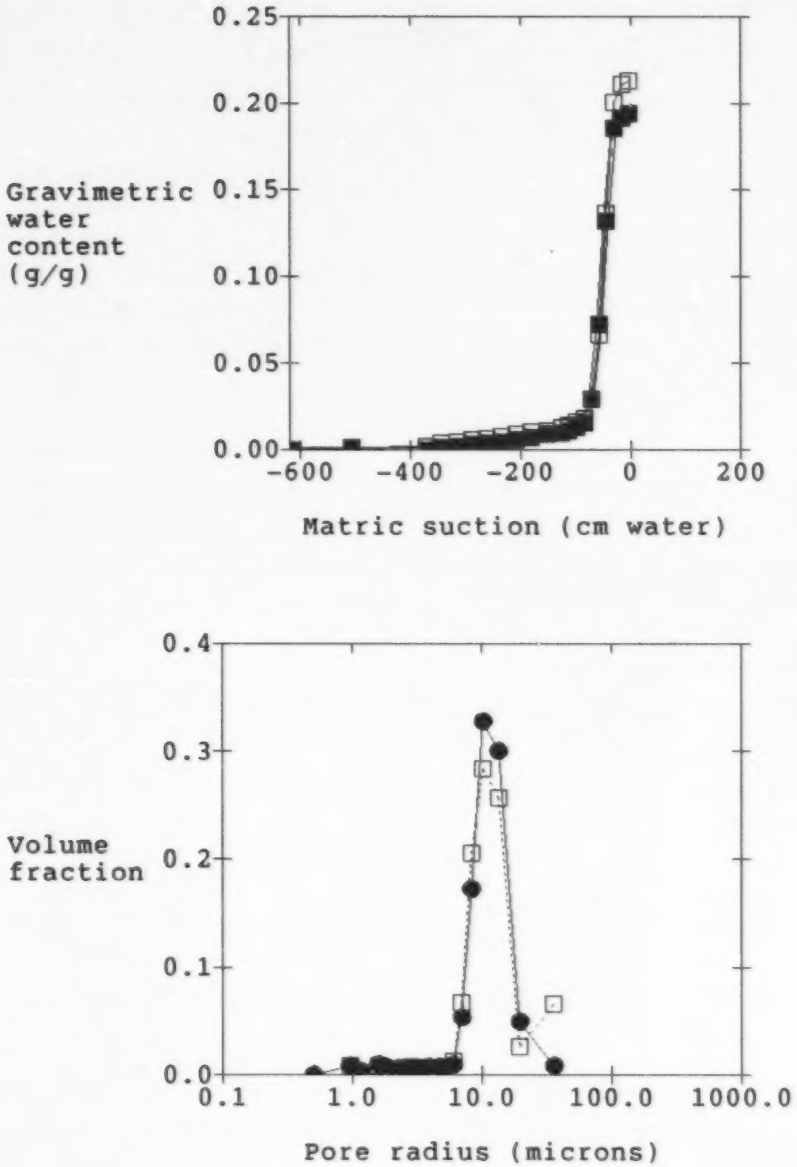


Figure 1. Soil moisture characteristic curves (replicates = 2) for Oil Creek sand (upper) and resultant pore size distribution (lower).

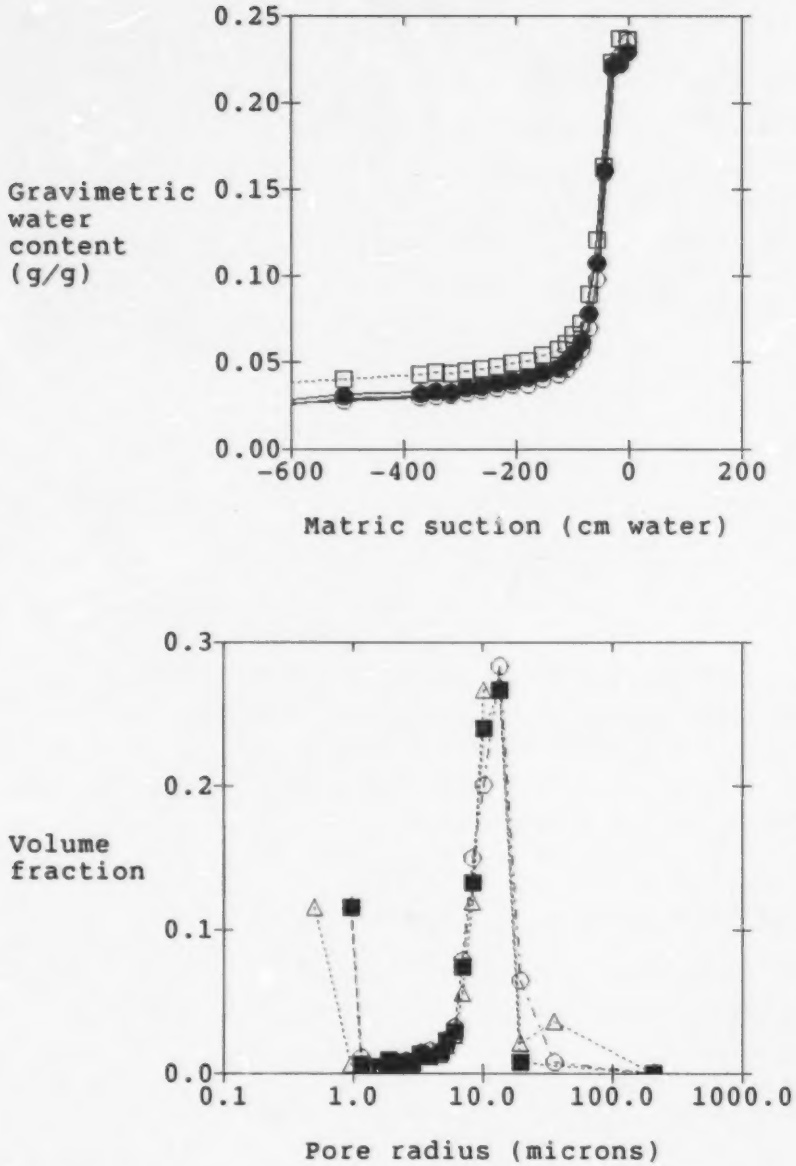


Figure 2. Soil moisture characteristic curves (replicates = 3) for amended Oil Creek sand (upper) and resultant pore size distribution (lower).

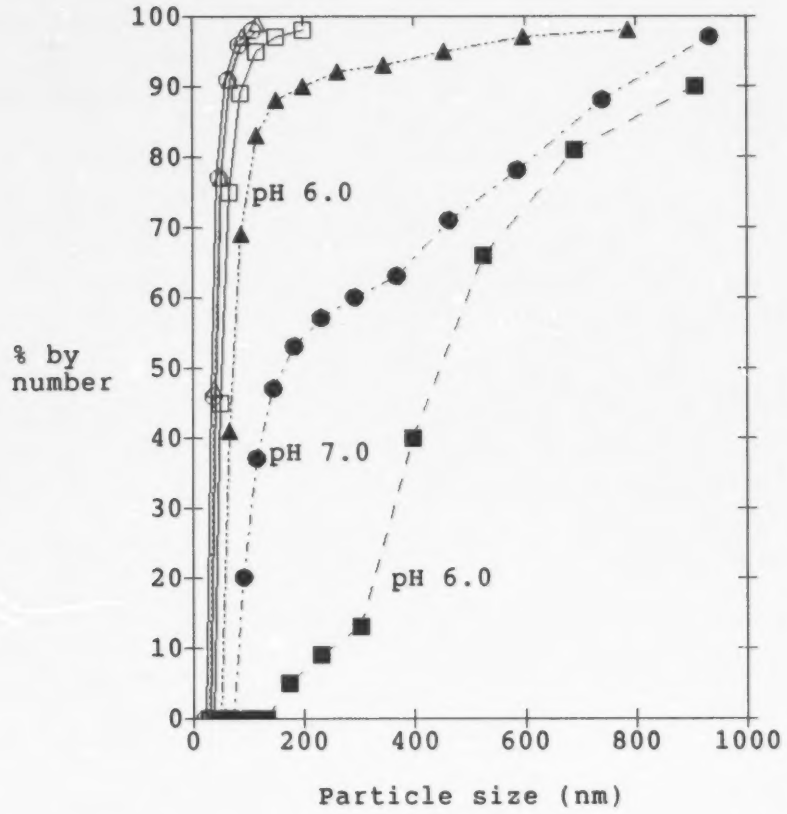


Figure 3. Cumulative particle size distribution of filtered humate muck (100 mg/l). Open symbols, distilled water; solid symbols, 0.001 M calcium chloride.

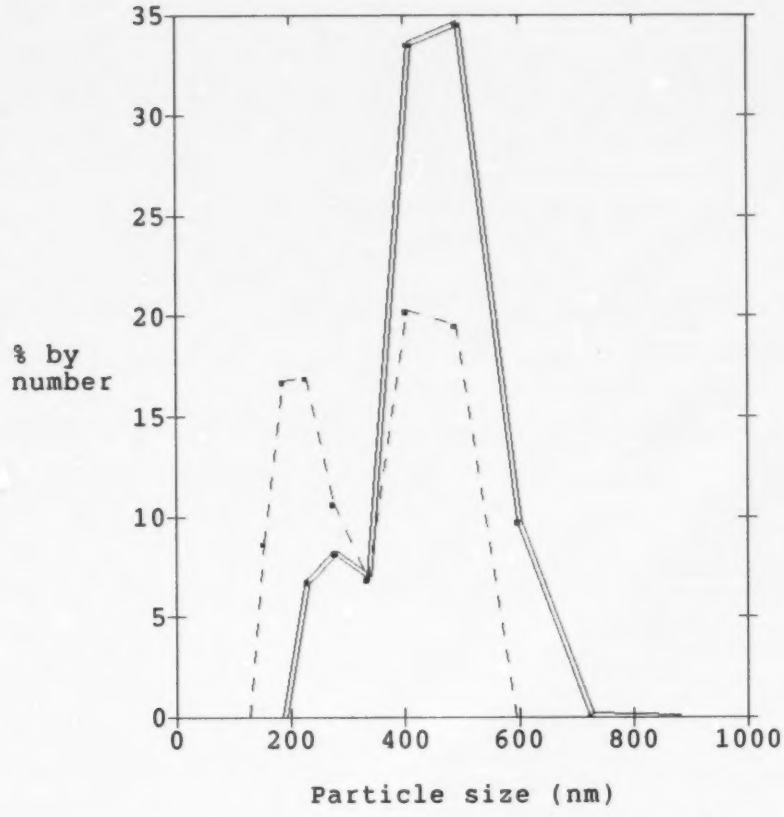


Figure 4. Particle size distribution for humate prepared in 0.01 M calcium sulfate (solid line) and 0.01 M sodium perchlorate (dashed line).

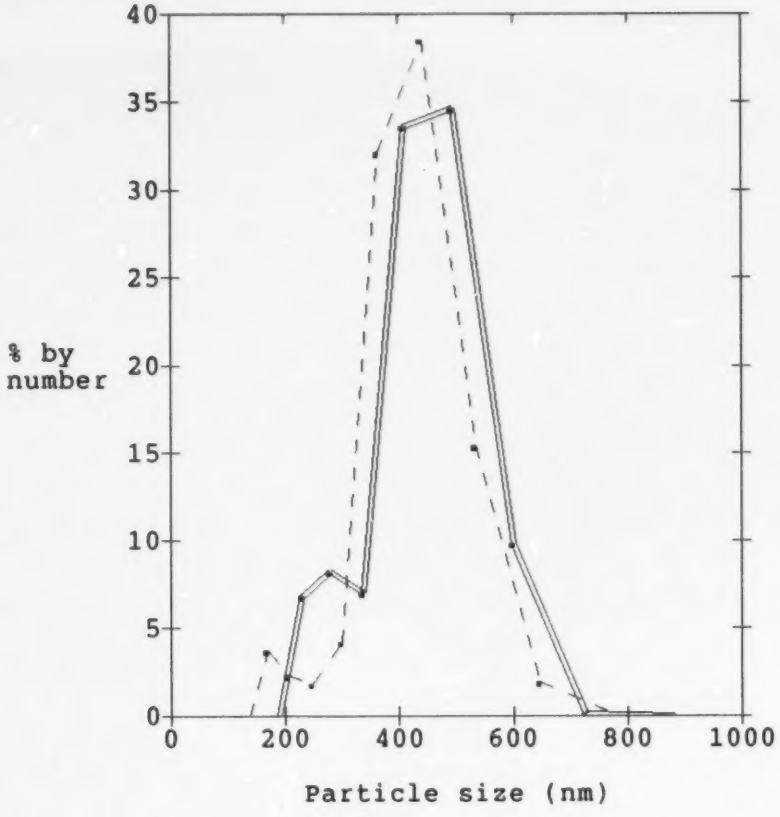


Figure 5. Particle size distribution stability of calcium humate. Time = 0 (solid line; distribution mean = 428 nm) and time = 5 days (dashed line; distribution mean = 407 nm).

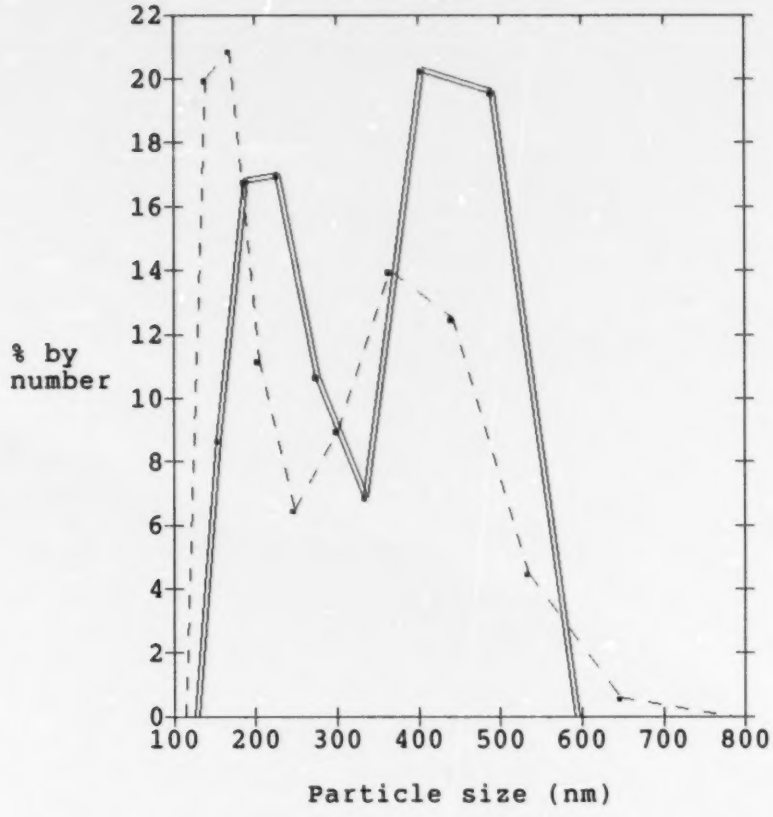


Figure 6. Particle size stability of sodium humate. Time = 0 (solid line; distribution mean = 314 nm) and time = 5 days (dashed line; distribution mean = 265 nm).

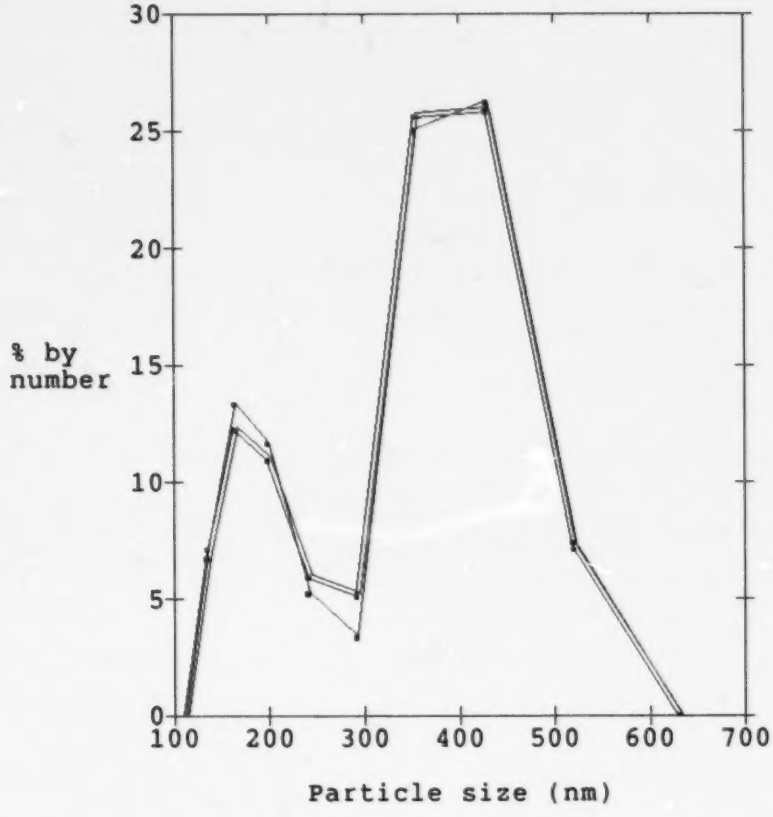


Figure 7. Reproducibility of particle size distribution of sodium humate. Batch #1, double line; batch #2, single line.

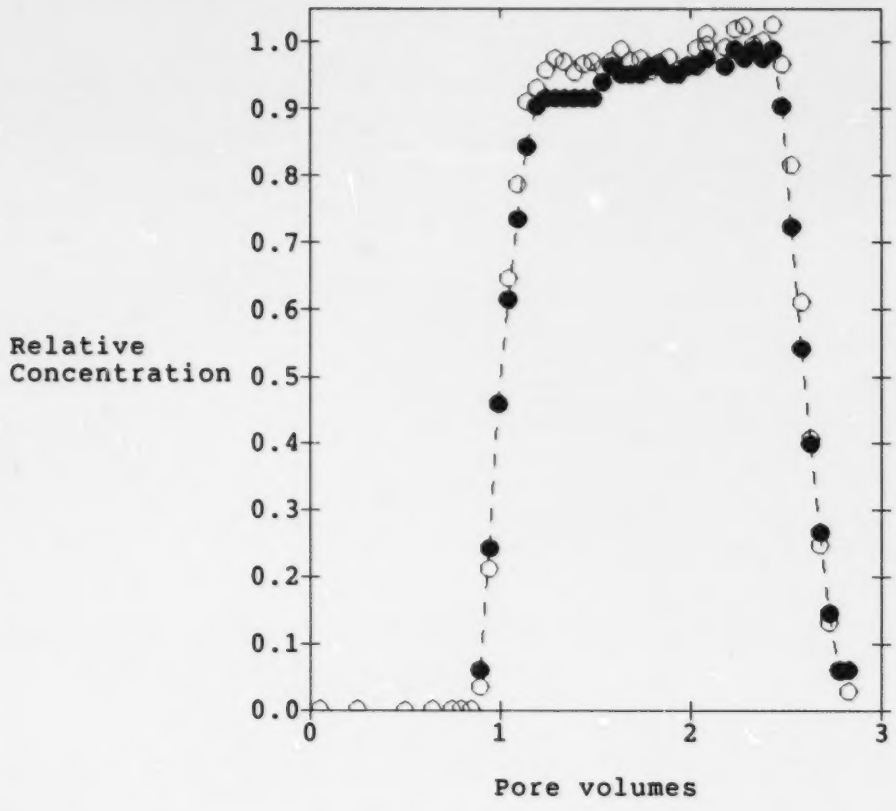


Figure 8. Blue dextran (solid circles) transport through Oil Creek sand. Tritiated water, open circles.

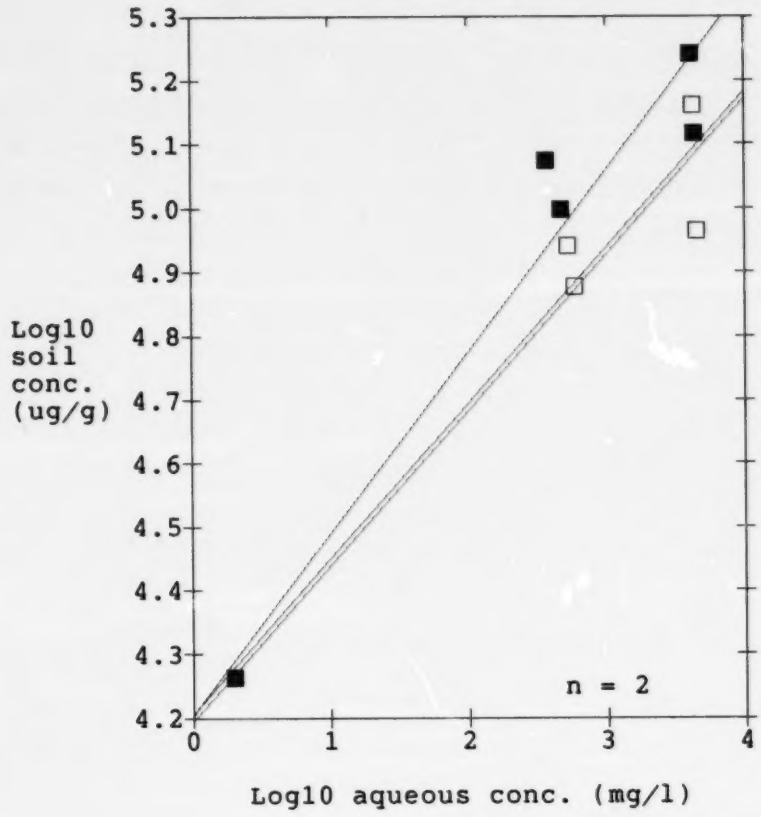


Figure 9. Freundlich sorption isotherm (log S =1/n (log C) + log Kp) for blue dextran to amended Oil Creek sand. At pH 4.0 (solid squares) 1/n = 0.28; log Kp = 4.2. At pH 8.0 (open squares) 1/n = 0.24; log Kp = 4.2. Samples were run at three concentrations at both pH's.

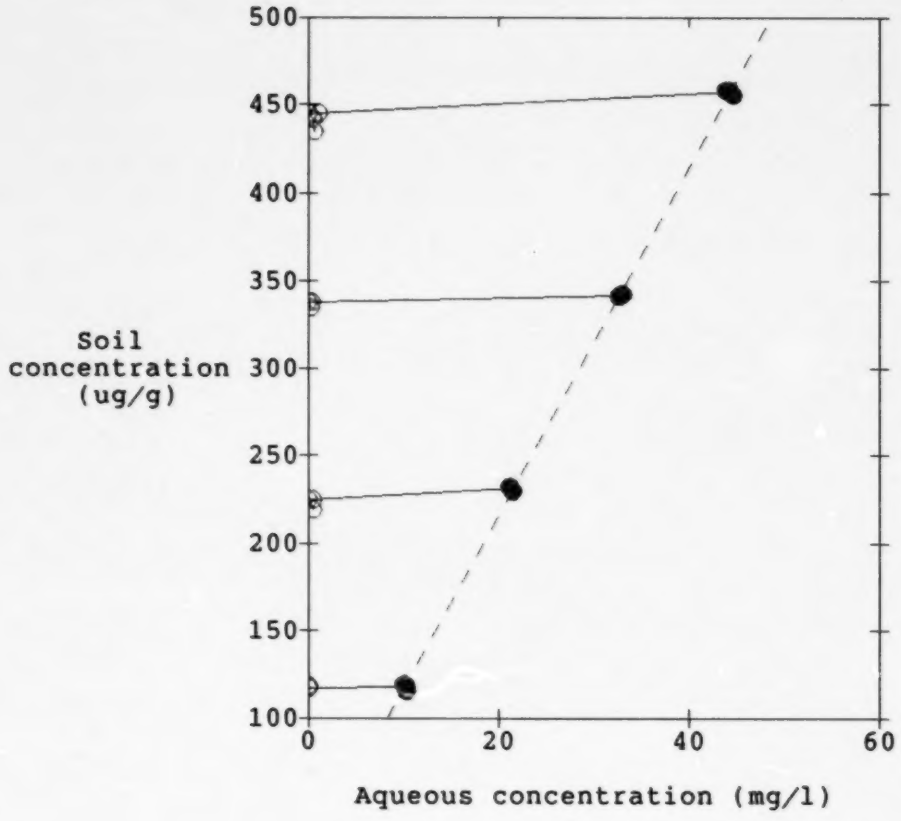


Figure 10. Sorption/desorption isotherm for cibacron blue to amended Oil Creek sand. Sorption data at 72 hours (solid circles; R-squared = 0.999); desorption data at 1,4,24,48 and 72 hours (open circles; average of triplicate samples).

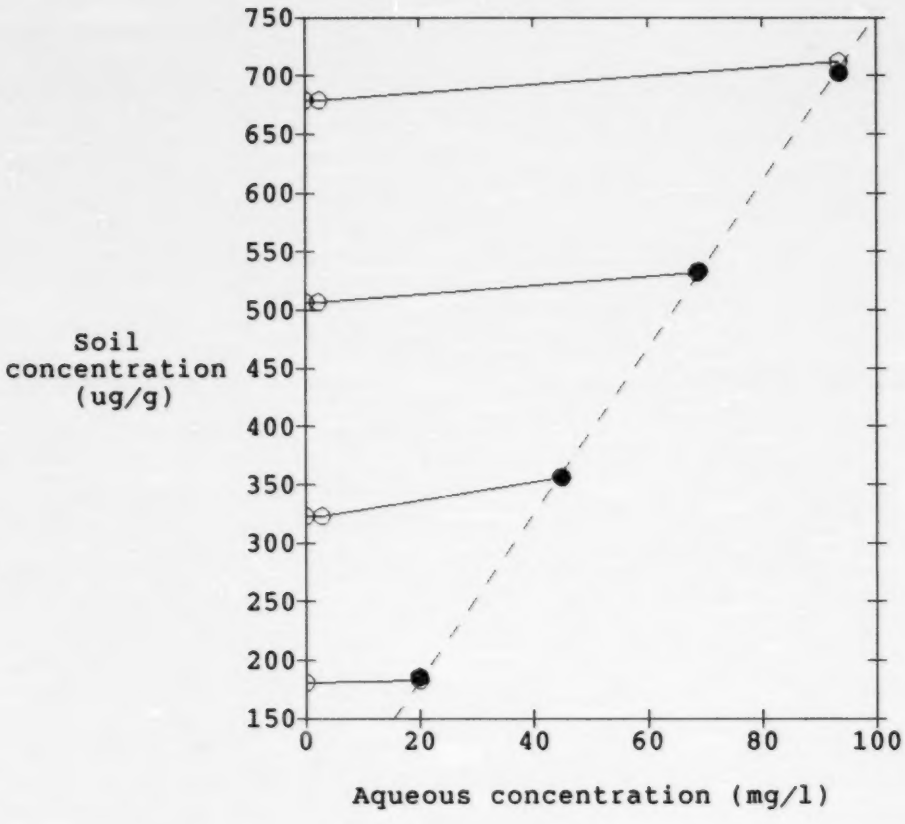


Figure 11. Sorption/desorption isotherm for dextran to amended Oil Creek sand. Sorption data at 72 hours (solid circles; R-squared = 0.999); desorption data at 3,6,24,48 and 72 hours (open circles; average of triplicate samples).

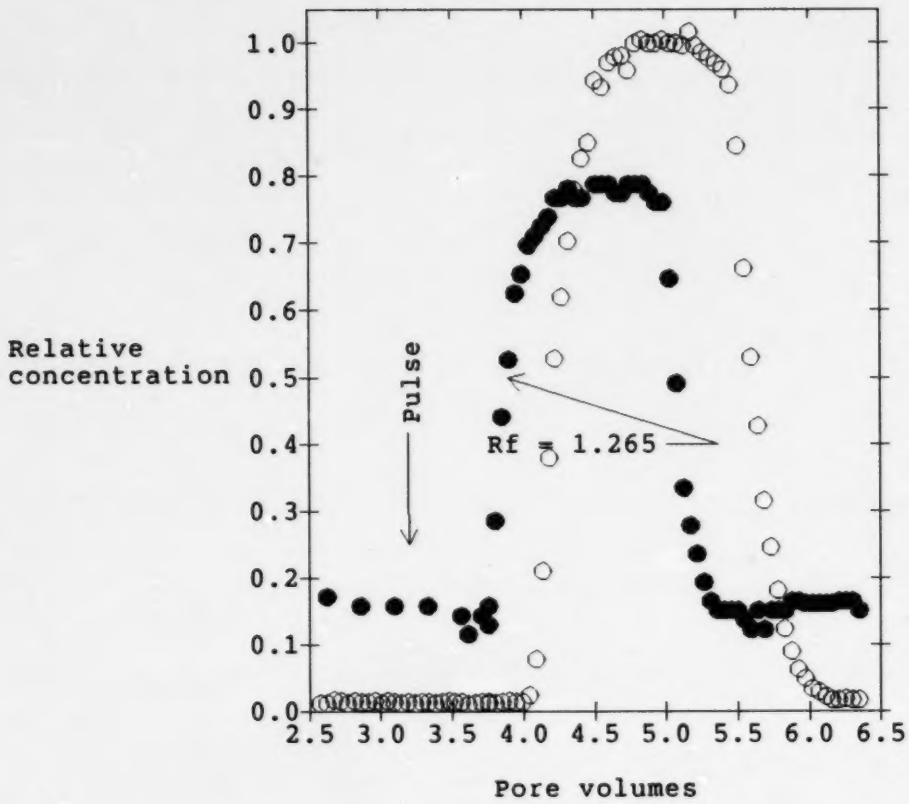


Figure 12. Blue dextran (solid circles) transport through amended Oil Creek sand after pre-saturation with blue dextran. Tritiated water, open circles.

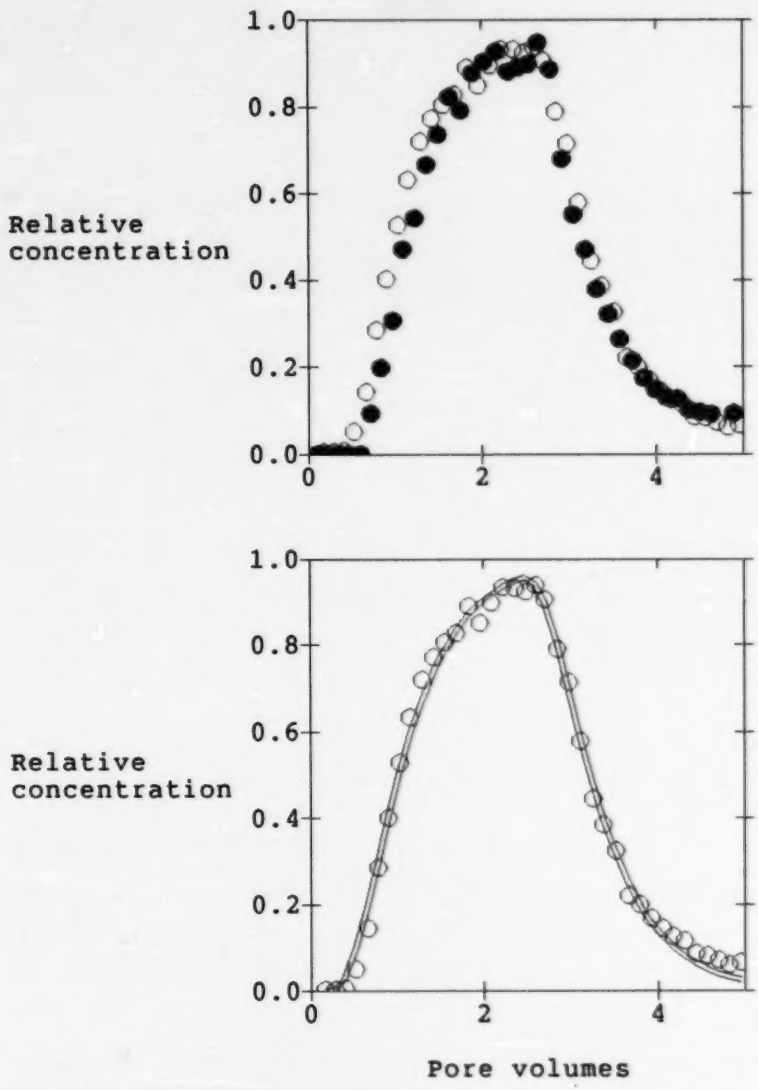


Figure 13. 770K poly(ethylene oxide) transport through Oil Creek sand (closed circles, top figure). Tritiated water data (open circles) was fitted using a non-linear least squares fitting procedure (double line, bottom figure). Porosity 0.32; dispersivity 0.16 cm, Darcy velocity 0.47 cm/hr.

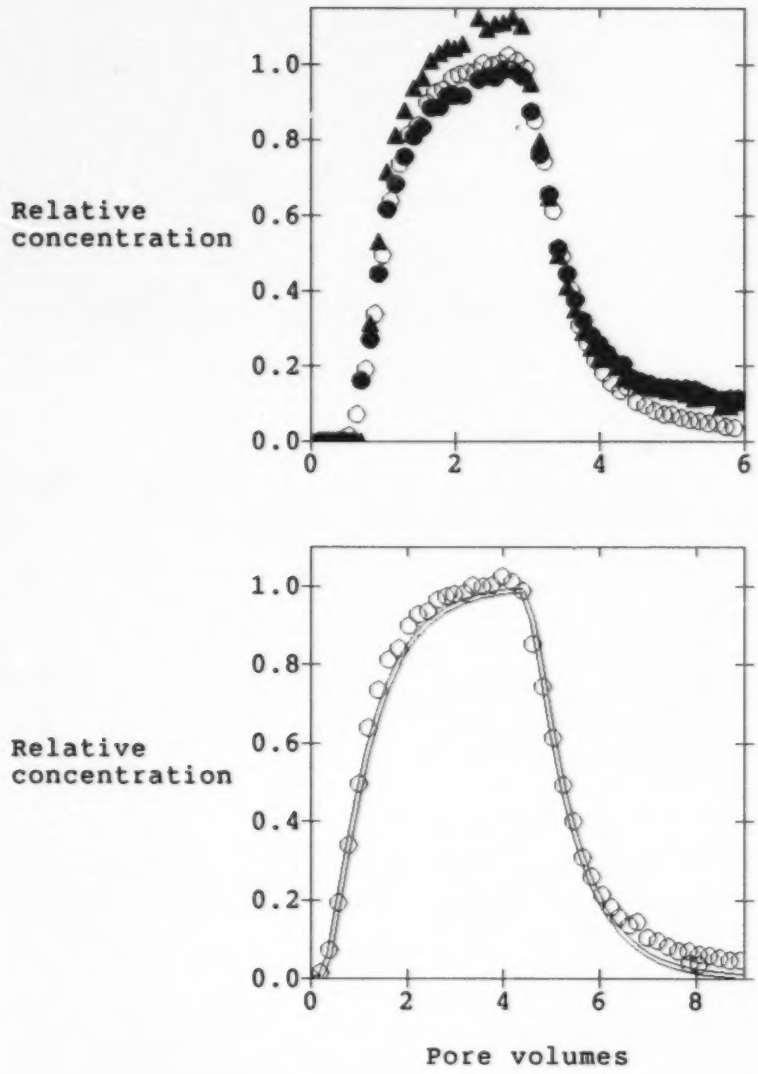


Figure 14. 900K and 83.8K poly(ethylene oxide) transport through Oil Creek sand (closed triangles and closed circles, respectively). Tritiated water data (open circles) was fitted using a non-linear least squares fitting procedure (double line, bottom figure). Porosity 0.32; dispersivity 0.27 cm; Darcy velocity 0.47 cm/hr.

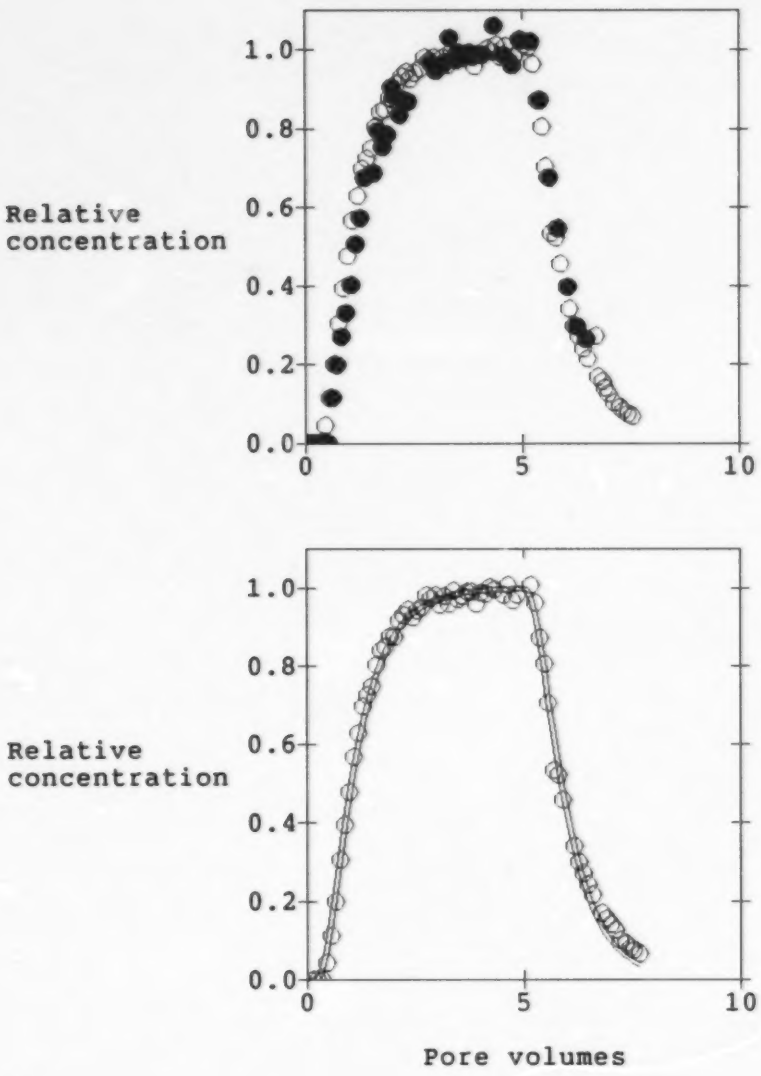


Figure 15. 50.4K poly(ethylene oxide) transport through Oil Creek sand (closed circles, top figure). Tritiated water data (open circles) fitted using a non-linear least squares procedure (double line, bottom figure). Porosity 0.32; dispersivity 0.21 cm; Darcy velocity 0.47 cm/hr.

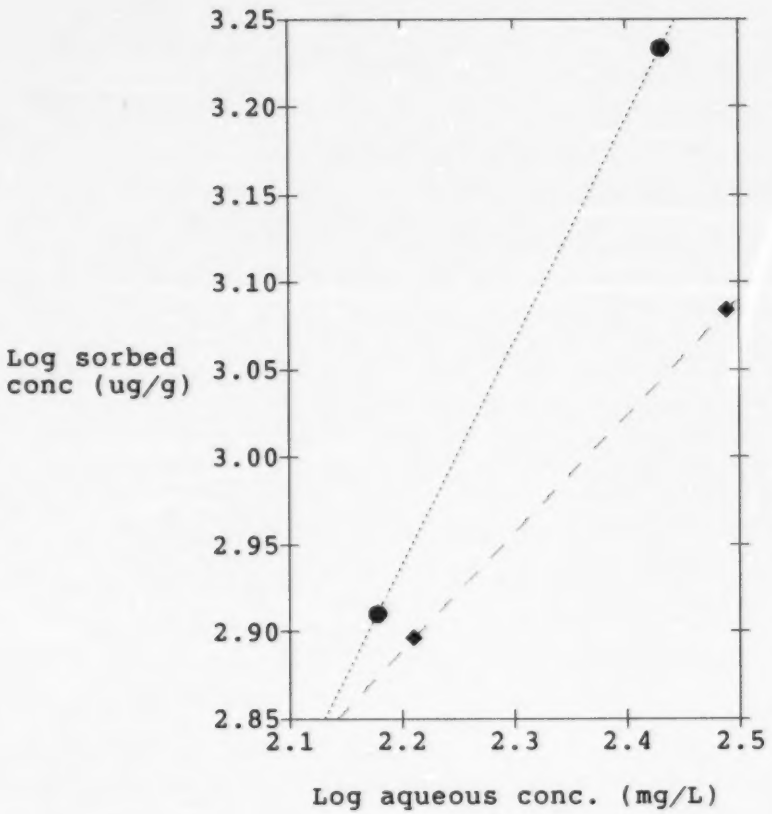


Figure 16. Freundlich sorption isotherm for 770K (diamonds; 1/n = 0.67; log Kp = 1.41) and 160K (circles; 1/n = 1.26; log Kp = 0.13) poly(ethylene oxides) to clay amended Oil Creek sand. All points are an average of triplicate samples.

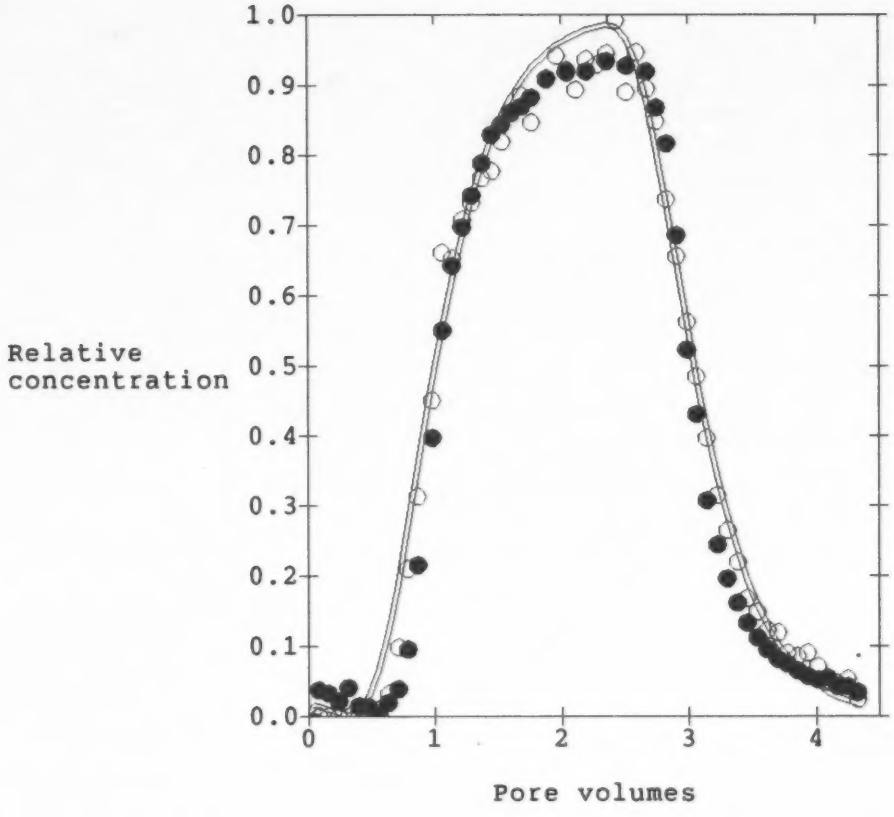


Figure 17. Calcium humate transport (closed circles) through Oil Creek sand. Tritiated water data (open circles) fitted by a non-linear least squares procedure (double line). Porosity 0.32; dispersivity 0.09 cm; Darcy velocity 0.47 cm/hr.

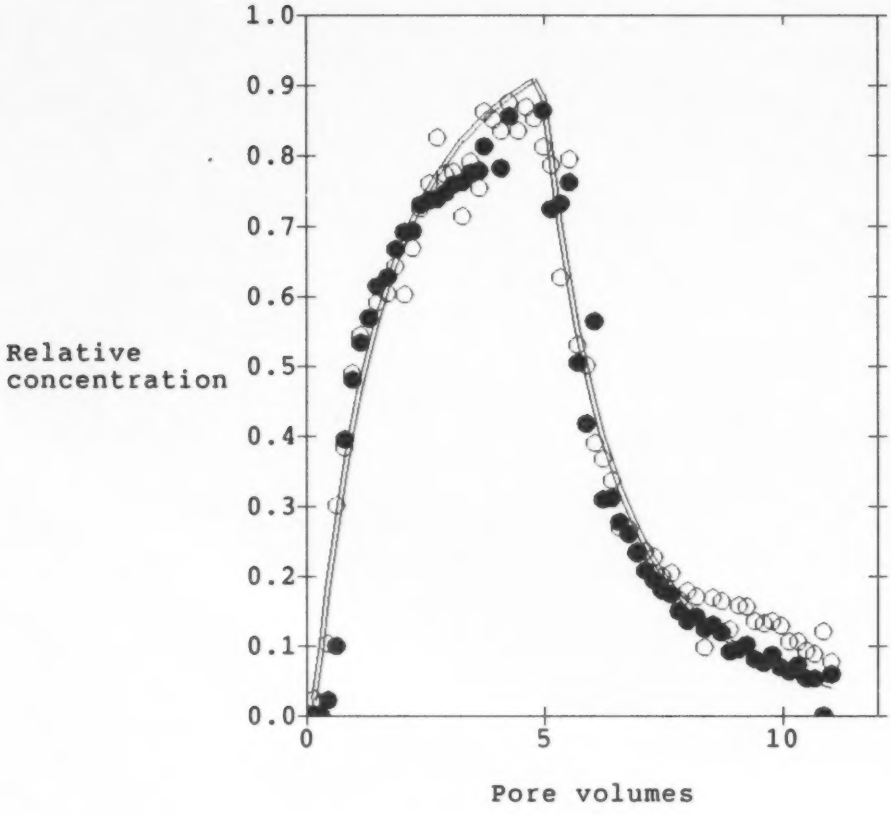


Figure 18. Sodium humate transport (closed circles) through Oil Creek sand. Tritiated water data (open circles) fitted by a non-linear least squares procedure (line). Porosity 0.32; dispersivity 1.2 cm; Darcy velocity 0.47 cm/hr.

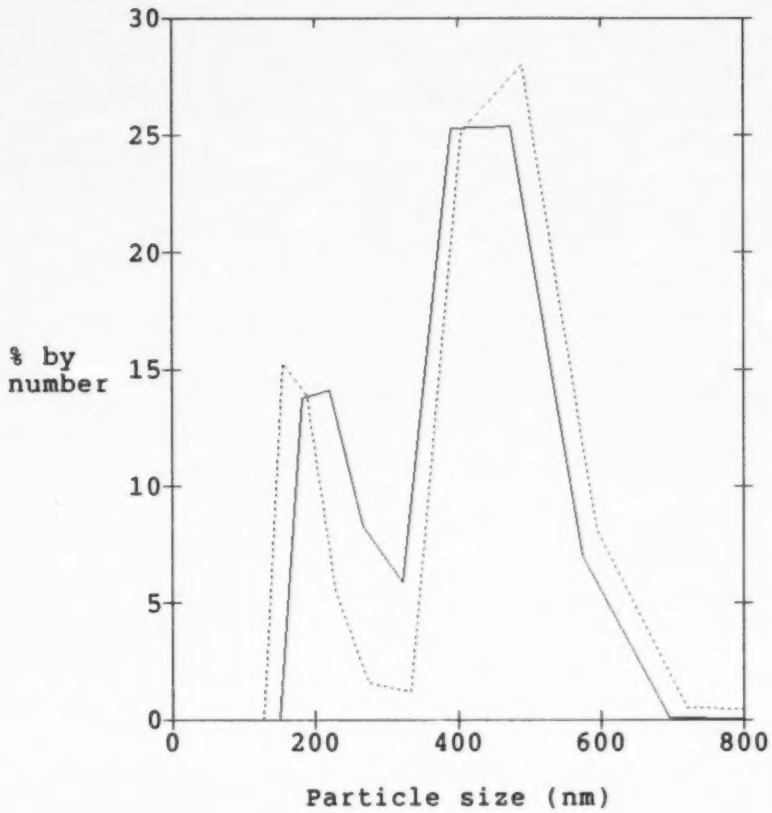


Figure 19. Particle size distribution of influent (solid line) and effluent (dashed line) of sodium humate transported through Oil Creek sand column.

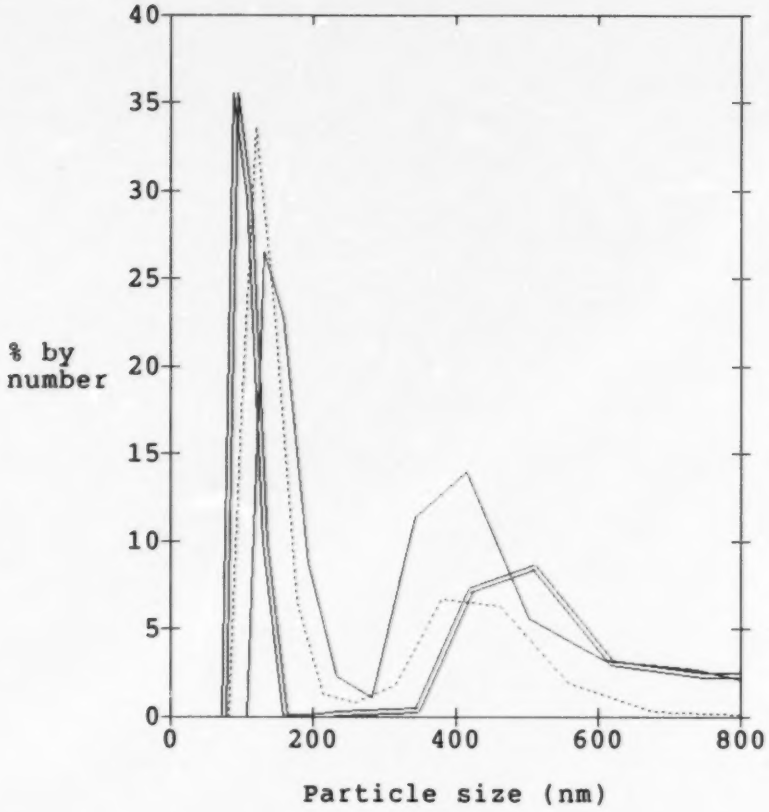


Figure 20. Particle size distribution of influent (single line) and effluent (double line, 1.0 pore volumes; dotted line, 1.9 pore volumes) of calcium humate transported through Oil Creek sand.

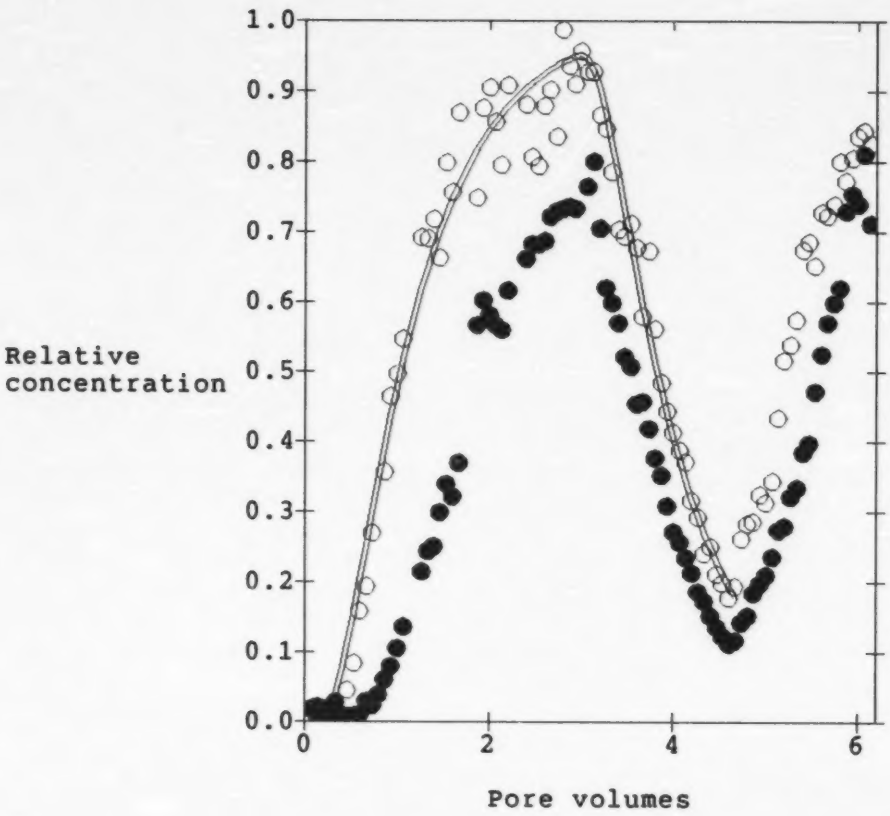


Figure 21. Calcium humate transport (closed circles) through amended Oil Creek sand. Tritiated water data (open circles) fitted by a non-linear least squares procedure (line). Porosity 0.32; dispersivity 0.26 cm; Darcy velocity 0.47 cm/hr.

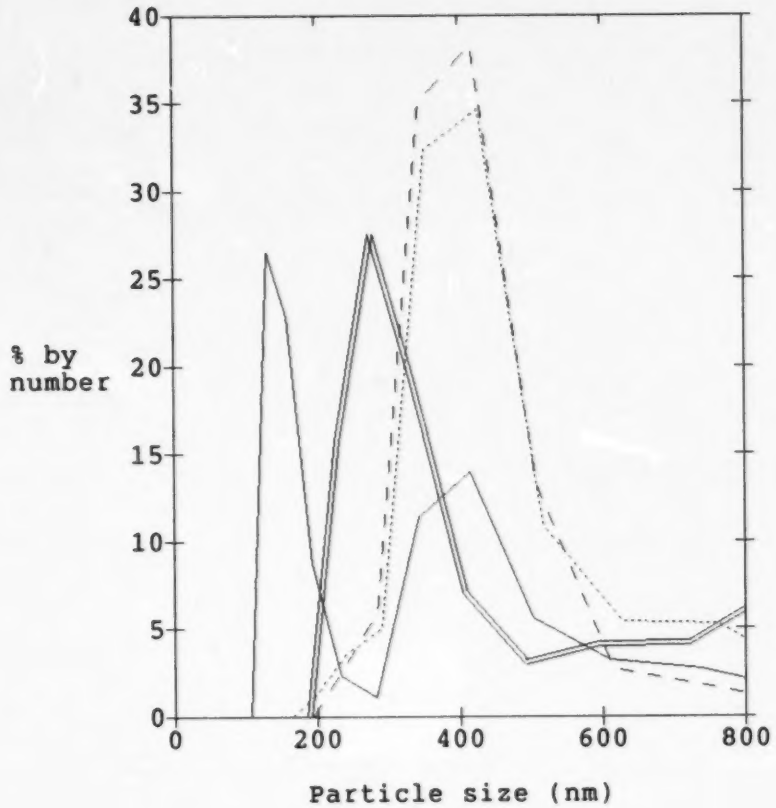


Figure 22. Particle size distribution of influent (solid line) and effluent (1.13, 1.73 and 2.27 pore volumes, double, dotted and dashed lines, respectively) of calcium humate transport through amended Oil Creek sand column.

Macromolecule	Conc. (ppm)	Primary particle size frequency distribution (nm)
Blue dextran	100	76
Poly(ethylene oxides)		
50,700 MW [1]	1261	ND [2]
83,800 MW	1119	190
770,000 MW	1044	140
900,000 MW	961	201
Humates		
$NaClO_4$/humate	327	200-250, 350-525
$CaSO_4$/humate	285	350-525

[1] Molecular Weight
[2] Not Determined

Table 1. Particle size frequency distribution for study macromolecules.

Macromolecule	Conc (ppm)	Column Packing	% Recovery	Observed Relative Velocity (Rf) [1]
Blue dextran				
	100	OCS [2]	98	1.00
	100	AOCS [3]	77	1.30
Poly(ethylene oxides)				
50,700 MW [4]	1261	OCS	95	0.86
83,800 MW	119	OCS	98	0.98
770,000 MW	1044	OCS	84	0.96
900,000 MW	961	OCS	109	1.12
Calcium humate				
	285	OCS	107	1.01
	320	AOCS	100	--
Sodium humate	325	OCS	96	0.98

[1] $R_f = (\bar{v}_p / \bar{v}_w)$
[2] Oil Creek sand
[3] amended Oil Creek sand
[4] molecular weight

Table 2. Concentrations, recoveries and relative velocities of study macromolecules.

References

Abdul, A.S., T.L. Gibson and D.N. Rai. 1990. Use of Humic Acid Solution to Remove Organic Contaminants from Hydrogeologic Systems. Environ. Sci. Technol. 24(3), pp. 328-333.

Bales, R.C., C.P. Gerba, G.H. Grondin and S.L. Jensen. 1989. Bacteriophage Transport in Sandy Soil and Fractured Tuff. Appl. Environ. Microbiol. 55(8), pp. 2061-2067.

Black, M.C. and J.F. McCarthy. 1988. Dissolved Organic Macromolecules Reduce the Uptake of Hydrophobic Organic Contaminants by the Gills of Rainbow Trout (*B Salmo Gairdneri*). Environ. Toxicol. Chem. 7, pp. 593-600.

Breger, I.A. 1970. What You Don't Know Can Hurt You: Organic Colloids and Natural Waters, In Organic Matter in Natural Waters, Inst. Mar. Sci. Occas. Pap. 1, edited by D.W. Hood, pp. 563-574, University of Alaska, College, Alaska.

Buddemeier, R.W. and J.R. Hunt. 1988. Transport of Colloidal Contaminants in Ground Water: Radionuclide Migration at the Nevada Test Site. Appl. Geochem. 3, pp. 535-548.

Cerda, C.M. 1988. Mobilization of Quartz Fines in Porous Media. Clays Clay Min. 36(6), pp. 491-497.

Chiou, C.T., D.E. Kile, T.I. Brinton, R.L. Malcolm, J.A. Leenheer and P. MacCarthy. 1987. A Comparison of Water Solubility Enhancements of Organic Solutes by Aquatic Humic Materials and Commercial Humic Acids. Environ. Sci. Technol. 21(12), pp. 1231-1234.

Clapp, C.E. and W.W. Emerson. 1972. Reactions Between Ca-Montmorillonite and Polysaccharides. Soil Science 114(3), pp. 210-216.

Degueldre, C., B. Baeyens, W. Goerlich, J. Riga, J. Verbist and P. Stadelmann. 1989. Colloids in Water from a Subsurface Fracture in Granite Rock, Grimsel Test Site, Switzerland. Geochimica et Cosmochimica Acta 53, pp. 603-610.

Dimarzio, E.A. and C.M. Guttman. 1969. Separation by Flow. Polym. Lett. 7, pp. 267.

DiMarzio, E.A. and C.M. Guttman. 1970. Separation by Flow. Macromolecules 3(2), pp. 131-146.

Enfield, C.G. and G. Bengtsson. 1988. Macromolecular Transport of Hydrophobic Contaminants in Aqueous Environments. Ground Water 26(1), pp. 64-70.

Ghosh, K. and M. Schnitzer. 1980. Macromolecular Structures of Humic Substances. Soil Science 129(5), pp. 266-276.

Gschwend, P.M. and M.D. Reynolds. 1987. Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Plume. J. Cont. Hydrol. 1, pp. 309-327.

Jirgensons, B. 1958. Introduction: The Scope of Organic Colloid Chemistry; Basic Terms, In Organic Colloids, edited by B. Jirgensons. pp. 3-9, Elsevier Publishing Company, Amsterdam, London, New York, Princeton.

Jones, K.C. and P.J. Peterson. 1989. Gold Uptake by Perennial Ryegrasses: The Influence of Humates on the Cycling of Gold in Soils. Biogeochem. 7, pp. 3-10.

Kan, A.T. and M.B. Tomson. 1990. Ground Water Transport of Hydrophobic Organic Compounds in the Presence of Dissolved Organic Matter. Environ. Toxicol. Chem. 9, pp. 253-263.

Kile, D.E. and C.T. Chiou. 1989. Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration. Environ. Sci. Technol. 23(7), pp. 832-838.

Lauzon, R.V. 1982. Water-Soluble Polymers for Drilling Fluids. Oil Gas J. April 12 Issue, pp. 93-98.

Leenheer, J.A., R.L. Malcolm, P.W. McKinley and L.A. Eccles. 1974. Occurrence of Dissolved Organic Carbon in Selected Ground-Water Samples in the United States. Jour. Research U. S. Geol. Survey 2(3), pp. 361-369.

McCarthy, J.F. and J.M. Zachara. 1989. Subsurface Transport of Contaminants. Environ. Sci. Technol. 23(5), pp. 496-501.

McDowell-Boyer, L.M., J.R. Hunt and N. Sitar. 1986. Particle Transport Through Porous Media. Water Res. Res. 22(13), pp. 1901-1921.

Murphy, E.M., S.N. Davis, A. Long, D. Donahue and A.J.T. Jull. 1989. Characterization and Isotopic Composition of Organic and Inorganic Carbon in the Milk River Aquifer. Water Res. Res. 25(8), pp. 1893-1905.

Nightingale, H.I. and W.C. Bianchi. 1977. Ground-Water Turbidity Resulting from Artificial Recharge. Ground Water 15(2), pp. 146-152.

Penrose, W.R., W.L. Polzer, E.H. Essington, D.M. Nelson and K.A. Orlandini. 1990. Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region. Environ. Sci. Technol. 24(2), pp. 228-234.

Peyton, G.R., J.P. Gibb, M.H. LeFaivre and J.D. Ritchey. 1985. On the Concept of Effective Porosity and Its Measurement in Saturated Fine-Grained Porous Materials, Illinois State Water Survey, Champaign, IL. (From 2nd Canadian/American Conference on Hydrology).

Peyton, G.R., J.P. Gibb, M.H. Lefaivre, J.D. Ritchey, S.L. Burch and M.J. Barcelona. 1986. Effective Porosity of Geologic Materials. In Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, Proceedings Report EPA/600/9-86/022.

Puls, R.W. and M.J. Barcelona. 1989. Filtration of Ground Water Samples for Metals Analysis. Hazardous Waste & Hazardous Materials 6(4), pp. 385-393.

Sakthivodiel. 1969. Clogging of a Granular Porous Medium by Sediment. HEL 15-7. Hydraulic Engineering Lab, University of Berkley. 109 pp.

Schnitzer, M., J.A. Ripmeester and H. Kodama. 1988. Characterization of the Organic Matter Associated with a Soil Clay. Soil Science 145(6), pp. 448-454.

Small, H. 1974. Hydrodynamic Chromatography - A Technique for Size Analysis of Colloidal Particles. J. Coll. Interface Sci. 48(1), pp. 147-161.

Smith, M.S., G.W. Thomas, R.E. White and D. Ritonga. 1985. Transport of *Escherichia Coli* Through Intact and Disturbed Soil Columns. J. Environ. Qual. 14(1), pp. 87-91.

Stoisits, R.F., G.W. Poehlein and J.W. Vanderhoff. 1976. Mathematical Modeling of Hydrodynamic Chromatography. J. Coll. Interface Sci. 57(2), pp. 337-344.

Stumm, W. 1977. Chemical Interaction in Particle Separation. Environ. Sci. Technol. 11(12), pp. 1066-1070.

Valsaraj, K.T. and L.J. Thibodeaux. 1989. Relationships Between Micelle-Water and Octanol-Water Partition Constants for Hydrophobic Organics of Environmental Interest. Wat. Res. 23(2), pp. 183-189.

Wershaw, R.L. 1986. A New Model for Humic Materials and Their Interactions with Hydrophobic Organic Chemicals in Soil-Water or Sediment-Water Analysis. J. Cont. Hydrol. 1, pp. 29-45.